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(54) Process for catalytic dewaxing of more than one refinery-derived lubricating base oil precursor.

<p>(30) Priority: 24.12.85 US 813214 (43) Date of publication of application: 23.09.87 Bulletin 87/39 (45) Publication of the grant of the patent: 03.06.92 Bulletin 92/23 (84) Designated Contracting States: BE DE ES FR GB IT NL SE (56) References cited: EP-A- 161 833 EP-A- 0 062 985 EP-A- 0 091 252 US-A- 4 211 635</p>	<p>(73) Proprietor: SHELL INTERNATIONALE RE- SEARCH MAATSCHAPPIJ B.V. Carel van Bylandtlaan 30 NL-2596 HR Den Haag(NL) (72) Inventor: Stem, Stephen Charles 3827 Redwood Falls Houston Texas 77082(US) Inventor: Winquist, Bruce Herman Charles 11202 Coldspring Drive Houston Texas 77043(US) Inventor: Bowen, James Ramsey 2140 Wilt Road Fallbrook California 92029(US)</p>
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Description

The invention relates to a process for catalytic dewaxing of more than one refinery-derived lubricating base oil precursor.

In the production of lubricating base oils from different distillates or deasphalted residual oils, a problem arises in regard to removing waxy materials from the lubricating base oil precursors. The presence of these waxy materials is very undesirable in that they inure a high pour point to the ultimate lubricating oil and thereby reduce or totally eliminate the effectiveness of the lubricating oil at low temperatures.

Two general methods for dewaxing these petroleum distillates include solvent dewaxing and catalytic dewaxing. The former has recently lost favour in light of its relatively high capital cost and its relatively high operating cost. The latter is sometimes referred to as hydrodewaxing and has been explored extensively. This technology has given rise to a whole new spectrum of catalysts which have been referred to by R.M. Barrer in his work, "Hydrothermal Chemistry of Zeolites" as tectosilicate catalysts which include aluminosilicates, borosilicates, etc. Essentially, it is desired to employ a tectosilicate catalyst with a pore size such that the long chain paraffin materials along with other waxy materials have selective access to the interior of the tectosilicate sieve while prohibiting entry of the non-waxy materials, which, of course, do not necessitate hydrodewaxing.

From a crude oil feed in many cases lubricating base oil precursors can be derived which are commonly classified as (Light) HVI 80 to 100 or 80 to 150, (Medium) HVI 250 to 300, (Heavy) HVI 500 to 600 and HVI Bright Stock raffinate (hereinafter referred to as Bright Stock), all of which necessitate dewaxing before they can be used as lubricating base oil (components).

Succinctly, there has not yet been developed a unitary tectosilicate or aluminosilicate catalytic composition which can selectively convert the paraffinic or other waxy materials in all of these petroleum substrates to selectively excise the problem waxy material and still attain the quality targets demanded by the marketplace. One reason for this dilemma is that the waxy materials, which are considered contaminants, vary greatly from stream to stream and are not simply straight-chain paraffins but include branched and cyclic structures as well. Thus, one catalyst with a specific consistent pore size will simply be unable to selectively treat all of the waxy materials present in all of these lubricating base oil precursors.

In U.S. Patent 4,222,855, issued in 1980, it was determined that a ZSM-23 or ZSM-35 catalyst possesses the ability to produce a dewaxed oil with a

superior viscosity index relative to a ZSM-5 type catalyst. This reference failed to teach or acknowledge however, that ZSM-35 is incapable of dewaxing an oil heavier than a light neutral to a pour point target currently demanded by the marketplace. Nor did it teach or acknowledge that this characteristic results from the special relationship between catalyst pore dimensions and the molecular structure of wax molecules intrinsic to lubricating oil streams of differing viscosity ranges. In U.S. Patent 4,372,839 recognition is made that a ZSM-35 catalyst alone is incapable of reducing the pour point to the most desired lowest level, however, this deficiency is resolved by a series flow technique of a common charge stream with both types of zeolites, i.e. a first contact with a ZSM-35 aluminosilicate and then a second with a ZSM-5 aluminosilicate.

Prior patentees have also taken cognizance of the fact that a feedstream to a hydrodewaxing unit may be divided and only a portion of the feedstream treated in a hydrodewaxing unit. For instance, in U.S. Patent 3,956,102, issued in 1976 to Chen et al, the patentees teach separation of a petroleum distillate whereby only one of the separated streams is treated with a ZSM-5 type catalyst while the untreated stream is subsequently combined with the hydrodewaxed product to yield a net production of hydrogen.

European patent application publication No. 161833 (EP 161833) discloses a dewaxing process in which process "heavy" and "light" charge stocks are contacted with different catalysts. In this document the "light" charge stock is defined by a 50% boiling-point of 454 °C and a kinematic viscosity at 100 °C of less than 9 cSt. However, this document fails to acknowledge the need to obtain and separately process two raffinate lubricating base oil precursors, where the separation is on the basis of the chemical nature of the waxy material present in the different lubricating base oil precursors. Especially the HVI 250-300 lubricating oils cannot be adequately dewaxed in the process disclosed in EP 161833.

An object of the invention is to provide a viable refinery dewaxing process flow scheme to selectively treat more than one refinery-derived lubricating base oil precursor in parallel flow in contrast to providing different catalysts in admixture in a single reactor which are respectively insufficient to treat one type of lubricating base oil precursor but highly efficient to treat another type of lubricating base oil precursor. Accordingly, a multiple number of dewaxed lubricating base oils having excellent pour points and viscosity indices can be obtained.

The invention therefore related to a process for catalytic dewaxing of more than one refinery-derived lubricating base oil precursor which com-

prises contacting in a first reaction zone in the presence of a hydrogen-containing gas at hydrodewaxing conditions a first feed stream comprising a first refinery-derived raffinate lubricating base oil precursor which contains a first wax comprising straight-chain paraffins, said first wax containing less than 55% by weight of branched and cyclic hydrocarbons, with a first hydrodewaxing catalyst selective for conversion of said first wax and contacting in the presence of a hydrogen-containing gas at hydrodewaxing conditions in a parallel situated second reaction zone a second refinery-derived raffinate lubricating base oil precursor which contains a second wax containing more than 55% by weight of branched and cyclic hydrocarbons with a second hydrodewaxing catalyst selective for conversion of said second wax, and optionally contacting in one or more further reaction zones further refinery-derived waxy raffinate lubricating base oil precursor feed streams in the presence of a hydrogen-containing gas at hydrodewaxing conditions with a hydrodewaxing catalyst, and removing at least two parallel effluent streams of refinery dewaxed lubricating base oils from said reaction zones.

Both of the types of catalyst utilized in the instant selective parallel passage hydrodewaxing process are existent in the prior art as known dewaxing catalysts. For instance, ZSM-5 type molecular sieve is disclosed in U.S. Patent 3,702,886 and taught for hydrodewaxing applications. Also, in U.S. Patent 4,343,692, a synthetic ferrierite zeolite is disclosed having incorporated therewith at least one metal selected from the group consisting of Group VIIB, Group VIIIB and Group VIIIIB metals. However, it has heretofore gone unrecognized that molecular sieves with pore dimensions similar to those of ferrierite are unable to dewax certain types of feed material to the specifications required by the marketplace but yet are surprisingly and unexpectedly effective in their conjunct interaction for selective parallel flow dewaxing of particular types of feed material when coupled into a process employing a dewaxing catalyst with pore dimensions similar to or larger than ZSM-5.

The process according to the invention suitably comprises three or more parallel operated catalytic hydrodewaxing zones.

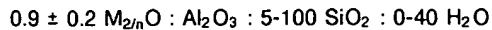
One embodiment of the invention resides in a process for the preparation of four or more dewaxed lubricating base oils from a crude oil feed stream which comprises: charging said crude oil feed stream to an atmospheric distillation column maintained at a pressure between 1.7 and 6.7 bar abs., at a bottoms temperature between 232 °C and 399 °C, and an overhead temperature of 204 °C to 316 °C to separate said crude oil feed stream into at least a light overhead stream, which

is withdrawn from said atmospheric distillation unit, comprising heavy gas oil and lighter hydrocarbons and a bottoms stream, which is removed from said distillation unit, comprising heavier than heavy gas oil hydrocarbons; withdrawing said heavy gas oil and lighter hydrocarbons and passing the same to another refinery unit for further processing; charging the bottoms effluent from said atmospheric distillation column containing heavier than heavy gas oil to a vacuum distillation column maintained at an overhead pressure between 0.02 and 0.09 bar abs. and at an overhead temperature from 38 °C to 93 °C and at a bottoms pressure from 0.13 bar abs. to 0.33 bar abs. and at a bottoms temperature between 316 °C and 399 °C to derive at least four raw lubricating oil process effluent streams comprising:

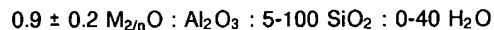
- i. a Light Vacuum Gas Oil overhead stream,
- ii. a High Viscosity Index 80-100 or 80-150 distillate,
- iii. a High Viscosity Index 250 to 300 distillate,
- iv. a High Viscosity Index 500 to 600 heavy distillate, and
- v. a bottoms stream containing residual distillate;

and then passing said bottoms stream residual distillate to a deasphalting unit wherein said residual distillate is contacted with a solvent to deasphalt said residual distillate to form an asphalt-rich stream and a deasphalted lubricating oil (DAO) stream; removing said asphalt-rich stream from said deasphalting unit; withdrawing said deasphalted lubricating oil (DAO) from said deasphalting unit; individually passing said HVI 80-100 or 80-150 distillate, HVI 250 to 300 distillate, HVI 500-600 distillate and said DAO hydrocarbon streams through a solvent extraction step wherein said solvent extraction step is performed separate and apart for each stream and passing the respective acquired solvent extracted HVI 80 to 100 or 80 to 150 waxy raffinate, HVI 250 to 300 waxy raffinate, HVI 500 to 600 waxy raffinate and wherein said DAO stream is converted to a Bright Stock waxy raffinate passed to a selective catalytic dewaxing step comprising: passing said HVI 80 to 100 or 80 to 150 waxy raffinate stream through a first catalytic dewaxing unit containing a catalyst comprising a synthetic ferrierite zeolite having incorporated therein at least one metal selected from the group consisting of Group VIIB, Group VIIIB and Group VIII metals of the Periodic Table to arrive at a substantially dewaxed HVI 80 to 100 or 80 to 150 stream having a pour point of below -4 °C, passing said solvent extracted HVI 250 to 300 waxy raffinate stream through a second catalytic dewaxing zone having therein a catalyst comprising an admixture of a synthetic ferrierite zeolite having incorporated therein at least one metal selected from the group consisting of Group VIIB, Group VIIIB and Group VIII

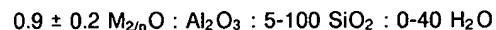
metals of the Periodic Table in association with a crystalline aluminosilicate zeolite having a composition in terms of mole ratios of, as follows:



wherein M is a cation, n is the valence of said cation and wherein said pore size of said zeolite is between 0.5 nm and 0.9 nm to arrive at a substantially dewaxed HVI 250 to 300 lubricating oil having a pour point of below -4 °C; passing said solvent extracted HVI 500 to 600 waxy raffinate stream through a third catalytic dewaxing zone having therein a catalyst comprising an admixture of a synthetic ferrierite zeolite having incorporated therein at least one metal selected from the group consisting of Group VIB, Group VIIB and Group VIII metals of the Periodic Table in association with a crystalline aluminosilicate zeolite having a composition, in terms of mole ratios, of as follows:



wherein M is a cation, n is the valence of said cation and wherein said pore size of said zeolite is between 0.5 nm and 0.9 nm to arrive at a substantially dewaxed HVI 500 to 600 lubricating oil having a pour point of below -4 °C; passing said Bright Stock waxy raffinate stream through a fourth aluminosilicate zeolite having a composition, in terms of mole ratios, of as follows:



wherein M is a cation, n is the valence of said cation and wherein said pore size of said zeolite is between 0.5 nm and 0.9 nm to derive a substantially dewaxed Bright Stock raffinate lubricating oil having a pour point of below -4 °C.

All of the aforementioned four respective lubricating base oil precursor streams contain different waxy contaminants, i.e. waxy components which elevate the pour point to a degree such that the oils are less attractive for their intended use. These streams differ in their molecular character and viscosity. It is also possible that but two streams are attained that necessitate dewaxing, usually (1) a light stream HVI 80 to 100 or 80 to 150 and (2) a heavy Bright Stock stream. It is also possible that three or more streams of different viscosities are derivable from such separatory systems. This invention pertains to treating in order to substantially dewax any two or more such streams in parallel flow arrangement.

In treating any of these streams various tectosilicate catalysts have been employed. One family of these tectosilicates are nomenclated as ZSM-5 aluminosilicate compositions which have been

characterized by their X-ray diffraction pattern as set forth in Table 1 of U.S. Patent 3,852,189, Chen et al.

Other catalysts are also contemplated as one of the catalytic compositions of matter useful in this invention. For instance, mordenites, crystalline borosilicates and silicalites may also be used. The mordenite may be modified by cation exchange including but not restricted to mordenites modified by cation exchange with H, Be, Mg, Ti, Ce, Nd, Pb, Th, Nb, Rh, Ba, Sr, La, and Ca. It also includes but is not restricted to mordenite modified by vapour deposition techniques employing compounds such as metal chlorides.

The second family of tectosilicate catalysts are those which selectively dewax relatively light lubricating oils such as an HVI 80 to 100 or 80 to 150 waxy raffinate in contrast to the above aluminosilicates which selectively dewax the heavier lubricating oils. One example of such catalyst is exemplified by the disclosure of Winquist U.S. Patent 4,343,692. Other such catalysts are ZSM-35, ZSM-23, ZSM-38, ZSM-21 and natural ferrierite, treated or untreated, with or without the presence of catalytic metals thereon.

It is also conceivable that both such catalysts are disposed on the same support and vary by the metals incorporated thereon, the strength of the acid sites, or by the cations incorporated into the support such that one catalyst will selectively react with the wax species characteristic of light lube stocks while the other catalyst selectively reacts with the wax species characteristic of heavier lube stocks.

While both of the aforementioned types of dewaxing catalysts have been known to adequately dewax certain feed materials, there has been no recognition that these two types of catalysts, used in conjunct simultaneous interaction, provide an unexpectedly more viable dewaxing process where a refiner is confronted with the dilemma of dewaxing a whole spectrum of differing lubricating oils. Two catalysts, one with pore dimensions similar to ferrierite and the other with pore dimensions equal to or greater than ZSM-5, will solve this dilemma because the wax species intrinsic to light lubricating oils is different form the wax species intrinsic to heavier lubricating oils.

The dewaxing step or steps of this invention are undertaken in the presence of hydrogen, preferably at a hydrogen circulation rate of between 350 and 2670 l(S.T.P.) H₂/l oil feed. The expression "S.T.P." indicates Standard Temperature (of 0 °C) and Pressure (of 1 bar abs.). The reaction conditions are usually maintained at a temperature of between 150 °C and 500 °C and a pressure between 2 and 200 bar abs., preferably between 2 and 20 bar abs. The liquid hourly space velocity

(LHSV) preferably will be from 0.1 to 10 and more preferably between 0.5 and 5.0.

The raw lubricating oils contemplated herein to be treated in parallel flow generally contain in the range of from 0.1 to 50% by weight of waxy hydrocarbons (by this latter term it is meant normally solid hydrocarbons at 3 °C below pour point temperatures). Pour point is defined on the basis of the ASTM D-97 Test Method. Example pour points for finished oils are -18 °C for HVI 80 to 100 or 80 to 150 and -7 °C for HVI Bright Stock. It is critical to the operation of this invention to properly select the particular feed material for the particular dewaxing catalyst. First inquiry must be made as to the type of undesired waxy hydrocarbons existent in the lubricating base oil precursor because it has been discovered that the type of waxy material present in the HVI 80 to 100 or 80 to 150 type of waxy raffinate lubricating base oil precursor is different from the waxy material indigenous to the HVI 250 to 300, HVI 500 to 600 or Bright Stock waxy raffinates. In fact, it comes as a surprise that those waxes intrinsic to raw lubricating oils heavier than HVI 80 to 100 or 80 to 150, contain a greater proportion of branched and cyclic structures than does HVI 80 to 100 or 80 to 150. It is indeed this discovery which accounts for the heretofore unrecognized problem with catalysts which have pore dimensions similar to ferrierite, i.e. they are unable to remove cyclic wax structures and, therefore, are incapable of dewaxing lube oil streams heavier than HVI 150 to the pour point demanded by the marketplace.

It is believed that the waxy materials present in HVI 80 to 100 or 80 to 150 lubricating oil have an average carbon number of 23 although the individual constituents of this stream are known to encompass a range of hydrocarbon components including minute quantities with 18 carbon atoms and 31 carbon atoms. It is believed that waxy materials present in HVI 250 to 300 have an average carbon number of 29 or 31 depending on the crude source. HVI 250 to 300 is known to encompass a range of hydrocarbon components including quantities of hydrocarbons with 24 carbons to 37 carbons. It is believed that the waxy hydrocarbons in HVI Bright Stock have an average carbon number of 38. HVI Bright Stock is known to encompass a range of hydrocarbon components which include quantities of hydrocarbons with 22 carbon atoms to 52 carbon atoms. The wax content of the first waxy raffinate (HVI 80 to 100 or 80 to 150) may have more than 45% by weight of normal paraffins in contrast to other waxy raffinate streams, such as HVI Bright Stock which may have less than 10% by weight of normal paraffin components. This concentration of normal paraffin wax structures is dependent on the crude oil feed charged to the unit.

It was surprising to find such a large content of branched and cyclic components in the heavy oil i.e. more than 55% by weight while the light oil contained less than 55% by weight of branched and cyclic components.

5 The complimentary independent parallel flow simultaneous interaction of the two catalysts for dewaxing, one with pore dimensions similar to ferrierite and the other with pore dimensions similar or larger than ZSM-5 will result in a reduction in the design size of particular dewaxing reactors, although more reactors may be necessary. The flexibility to cease dewaxing over one type of catalyst (while the other continues to simultaneously function) and perform select reactivation prior to reaching high end-of-run temperatures will significantly and surprisingly result in a greatly lengthened viable life span of the large pore catalyst without the penalty of lost production. Also, by avoiding a complete shutdown of the plant as a result of catalyst reactivation the overall dewaxing plant can have a smaller design, be constructed with less offsite tankage and be designed with less catalyst inventory for each reactor. If a plant error occurs and a contaminant like sodium, for example, is allowed into one reactor, the other may continue to function unimpeded. And if the crude oil feed of the refinery changes, the market target projections can still be maintained due to the flexibility of the complimentary catalysts.

10 In this parallel passage flow system a continuous operation of dewaxing is contemplated and preferred. When a certain catalyst becomes deactivated due to occlusion by trapped hydrocarbons or weakly held catalyst poisons it is a simple procedure to cease the dewaxing step and begin a hydrogen reactivation of the catalyst. This hydrogen reactivation is performed in the presence of a hydrogen-containing gas at a temperature between 343 °C and 538 °C. One dewaxing catalyst can be reactivated or regenerated while other dewaxing catalysts continue to perform their respective catalytic function until they too become spent and thereby necessitate reactivation.

15 An oxidative regeneration of the catalyst may be undertaken in situ or more preferably the regeneration may be performed at an offsite location in a separate regeneration vessel by passage of an oxygen-containing gas thereover at a temperature from 371 °C to 566 °C for a period of time sufficient to remove coke deposits and thereby regenerate the dewaxing catalyst. Thereafter the regenerated catalyst is passed back to its respective dewaxing reactor vessel. The oxygen-containing gas can be air, pure oxygen or mixtures of oxygen with any other inert gas such as nitrogen or argon.

20 It is contemplated within the scope of this

invention to treat at least two, and even four lubricating base oil precursor streams derived from a vacuum distillation unit as described hereinbefore. However, these streams can be commingled within the scope of this invention as long as at least two different catalysts are applied in parallel flow reaction zones for converting the particular undesired waxy materials present therein. It is also contemplated that downstream of the overall catalytic dewaxing process, established techniques, including clay treating and hydrofinishing, can be used to enhance the colour and stability of the dewaxed oil. It is further contemplated that downstream of the overall catalytic dewaxing process, normal blending techniques can be utilized to prepare any type of lubricating base oil or industrial oil, such as an automotive engine oil, transformer oil, compressor oil, railroad oil, refrigerator oil, hydraulic oil, gear oil, or any other lubricant necessitating specific qualities of pour point at a certain temperature.

The invention also relates to catalytically dewaxed lubricating base oils whenever prepared by a process as described hereinbefore.

In the Figure a flow scheme is depicted which is exemplary of the production of four different dewaxed lubricating base oils beginning from a crude oil feed material although the process scheme can be used with as few as two respective lubricating oil streams.

The instant flow scheme is given without regard to miscellaneous auxilliary equipment necessary to perform the process flow such as various pumps, condensers, receivers and so forth. The process flow scheme is not to be construed as a limitation upon the instant novel parallel flow process. In the Figure a crude oil in conduit 1 is charged to fractionation column 3 wherein a light product stream is withdrawn through conduit 5, either overhead or as a sidecut stream or both, and is removed from the process and passed along for further processing to recover other hydrocarbon minerals. The bottoms stream from fractionation column 3 is withdrawn through conduit 7 and passed to vacuum distillation unit 9. This stream contains all of the material heavier than a heavy gas oil. In the vacuum distillation column up to five streams are derived with the overhead stream being withdrawn in conduit 11 having an initial boiling point of about 238 °C and a 50% boiling point of about 354 °C, which also may be further processed according to known conventional processing techniques for its mineral value. Three streams are exemplified as being withdrawn from the vacuum distillation unit as sidecut streams HVI 80 to 100 or 80 to 150, HVI 250 to 300 and HVI 500 to 600 raw undewaxed distillates containing waxy material which result in a pour point of such a mag-

nitude to vitiate target projection of the open lubricating oil marketplace. An HVI 80 to 100 or 80 to 150 distillate stream is withdrawn via conduit 13, an HVI 250 to 300 distillate stream is withdrawn via conduit 15 and an HVI 500 to 600 distillate stream is withdrawn via conduit 17. A fifth stream, withdrawn from the bottom of vacuum distillation unit 9 via conduit 19, contains heavy materials, such as asphalt and residua. This stream is passed to deasphalting unit 21 wherein an asphalt-rich product is withdrawn in conduit 23 concomitant with the deasphalted oil withdrawn in conduit 25. This stream commonly nomenclated as (DAO) also has indigenous undesirable waxy material which raises the pour point of the lubricating oil to a degree to render same unsuitable for most commercial use.

It is optional in this invention to utilize a preliminary solvent extraction system to treat the waxy lubricating oil distillates. The solvent is any conventional extraction solvent such as phenol, N-methyl-2-pyrrolidone, furfural, etc. These solvent streams are added to respective batch extraction units 27, 29, 31 and 33 through conduits 35, 37, 39, and 41. A slip stream or bottom contaminant stream is withdrawn containing extracted aromatics, nitrogen and sulphur compounds in streams 43, 45, 47 and 49, which may likewise be treated in a distillation column (not shown herein) for return of the solvent to the solvent extraction system(s). This is also true for a portion or the entirety of streams 51, 53, 55 and 57. It is important to note that this solvent extraction system can be performed in a batch type method in a multitude of zones or the same can be performed in one zone, one-at-a-time, with only one respective particular waxy raffinate stream derived from the vacuum distillation column being solvent extracted at one time. The respective effluent streams from the solvent extraction zone in conduits 51, 53, 55 and 57 are passed into optional hydrotreating systems 59, 61, 63 and 65 which have ingress of hydrogen through conduits 67, 69, 71 and 73. While these hydrotreaters are shown as different units, they may physically be one integrated vessel useful for treating a multitude of streams. It is also contemplated that the hydrotreating be performed before the solvent extraction. Either way, the pre-dewaxing hydrotreating zone is purely optional and its presence or placement does not form an integral process parameter of the instant flow scheme contemplating the dual bed parallel passage flow of lubricating base oil precursors to different hydrodewaxing catalysts.

The function of the hydrotreater is to excise additional aromatic compounds, sulphur compounds, nitrogen compounds and convert complex aromatic compounds to simpler aromatic compounds which renders the catalytic dewaxing processing more feasible. Hydrotreating is performed

at mild hydrotreating conditions, which include a temperature of from 260 °C to 454 °C and a pressure from 74 bar abs. to 107 bar abs. The hydrogen may be present concomitant with an inert gas or the same may be present in its pure form. It is also contemplated that a refinery stream such as a reformer gas stream may be utilized as the source of hydrogen. Once again, however, it should be pointed out that this pre-dewaxing hydrotreatment step is optional, and need not be performed to accomplish the goals of this invention. The solvent extracted, or if desired, hydrotreated effluent streams, are withdrawn from respective (or one single hydrotreater operating in blocked out mode) from hydrotreaters 59, 61, 63 and 65 through conduits 75, 77, 79 and 81. They are passed directly to the respective appropriate catalytic dewaxing steps 83, 85, 87 and 89, which are provided with hydrogen entry ports 91, 93, 95 and 97. The respective dewaxed lube oils are withdrawn from respective catalytic dewaxing units (or as few as two units) 83, 85, 87 and 89 through conduits 99, 101, 103 and 105 for further blending.

After production of these streams hydrotreating is normally undertaken to further refine the finished dewaxed product. One salient advantage of this invention is that use of ferrierite catalyst in dewaxing zone 83 totally obviates the need to hydrotreat the product in conduit 99 after blending with other feed streams. Rendering this expensive and potentially troublesome extra process step superfluous surprisingly produces an overall process much more efficient and less expensive than any other type process which requires that the dewaxed light oils are to be hydrotreated. If desired, the light oil dewaxed effluent stream may be hydrotreated within the scope of this invention although, to do so is a processing of the dewaxed oil in a non-economically rewarding sequence of steps. In summary, this process produces a light HVI 80 to 100 or 80 to 150 lubricating base oil using a more efficient catalyst without the necessity for hydrotreating, in the presence of hydrogen, the dewaxed oil concomitant with other heavy dewaxed oils which may necessitate dewaxing.

Another embodiment of this invention comprises the passage of the DAO stream directly from deasphalting unit 21 to hydrotreater 65 without need for the solvent extraction step, said pre-dewaxing hydrotreating being carried out at mild to severe hydrotreating conditions, i.e. over 74 bar abs. pressure and over 260 °C. Hydrotreated effluent is passed via conduit 81 to catalytic dewaxing unit 89 for aforementioned treatment.

It is also optional in this invention to utilize a preliminary solvent dewaxing system to treat the waxy lubricating oil raffinates, especially those requiring very low pour points, for example below -18

°C. The solvent is any conventional dewaxing solvent such as propane, or alkyl ketones in admixture with an aromatic component, i.e. methylethyl ketone and toluene. These streams may be added in a batch processing manner. The solvent may be recovered by distillation and reused in the solvent dewaxing process. This preliminary solvent dewaxing can be performed in a multitude of zones or the same can be performed in one zone using a batch-type method one-at-a-time with each such particular waxy raffinate derived from the vacuum distillation column.

The preferred catalyst in hydrogen dewaxing unit 83 is one with a pore size similar to the pore size of synthetic ferrierite. The preferred catalyst of hydrogen dewaxing unit 89 (for the Bright Stock waxy raffinate) is a catalyst with a pore size similar or larger than the pore size of the ZSM-5 catalyst taught in U.S. Patent 3,702,886. The latter can also be used in hydrogen dewaxing units 85 and 87 with or without accompaniment of a smaller pore zeolite. Again, the use of the preferred ferrierite-containing catalyst obviates post-dewaxing hydrotreatment.

The process conditions present in the fractionation column 3 or 9, deasphalting unit 21, solvent extraction units 27, 29, 31, 33 and the hydrotreating units 59, 69, 71 and 73 are well known to those of reasonable skill in the art. Hydrotreating conditions and applicable catalysts for hydrotreating streams 101, 103, 105 or same if combined with stream 99, are likewise well-recognized. The process conditions present during the hydrodewaxing steps in reactors 83, 85, 87 and 89 are those alluded to previously above. It will not require any type of expertise or undue experimentation for one to ascertain the most desirable conversion conditions once the feed material is selected for the particular catalytic composition of matter of respective units 83, 85, 87 and 89.

Claims

1. A process for catalytic dewaxing of more than one refinery-derived lubricating base oil precursor which comprises contacting in a first reaction zone in the presence of a hydrogen-containing gas at hydrodewaxing conditions a first feed stream comprising a first refinery-derived raffinate lubricating base oil precursor which contains a first wax comprising straight-chain paraffins, said first wax containing less than 55% by weight of branched and cyclic hydrocarbons, with a first hydrodewaxing catalyst selective for conversion of said first wax and contacting in the presence of a hydrogen-containing gas at hydrodewaxing conditions in a parallel-situated second reaction zone a sec-

ond refinery-derived raffinate lubricating base oil precursor which contains a second wax containing more than 55% by weight of branched and cyclic hydrocarbons with a second hydrodewaxing catalyst selective for conversion of said second wax, and optionally contacting in one or more further reaction zones further refinery-derived waxy raffinate lubricating base oil precursor feed streams in the presence of a hydrogen-containing gas at hydrodewaxing conditions with a hydrodewaxing catalyst, and removing at least two parallel effluent streams of refinery dewaxed lubricating base oils from said reaction zones.

2. A process according to claim 1 wherein the lubricating base oil precursor feed streams are obtained by fractionating a bottoms stream of an atmospheric distillation of a hydrocarbon oil feed stream.

3. A process according to claim 1 or 2 wherein the hydrodewaxing conditions comprise a temperature between 150 °C and 500 °C, a pressure between 2 and 200 bar abs. and a hydrogen/oil feed ratio between 350 and 2670 l (S.T.P.) H₂/l oil feed.

4. A process according to any one of the preceding claims wherein the first hydrodewaxing catalyst comprises a synthetic ferrierite having incorporated therewith at least one metal selected from the group consisting of Group VIB, Group VIIB and Group VIII metals of the Periodic Table.

5. A process according to claim 4 wherein a first feed stream comprising an HVI 80 to 150 or 80 to 100 waxy lubricating oil precursor is hydrodewaxed in the first reaction zone from which a lubricating base oil is obtained without subsequent hydrotreating.

6. A process according to any one of the preceding claims wherein the second hydrodewaxing catalyst comprises a crystalline aluminosilicate having a pore size from 0.5 to 0.9 nm and a composition, in terms of mole ratios, as follows:

0.9 ± 0.2 M_{2/n}O: Al₂O₃:5-100 SiO₂:0-40 H₂O

wherein M is a cation and n is the valence of said cation.

7. A process according to any one of the preceding claims which comprises at least three, and preferably four or more parallel situated cata-

lytic hydrodewaxing zones.

8. A process according to any one of the preceding claims wherein each hydrodewaxing catalyst is regenerated independently of the dewaxing operation(s) in the other dewaxing reaction zone(s) in the presence of an oxygen-containing gas at a temperature from 371 °C to 566 °C.

9. A process according to claim 8 wherein said regeneration is followed by an inert gas purge of the regenerated catalyst and subsequent reactivation in the presence of a hydrogen-containing gas at a temperature from 343 °C to 538 °C.

10. A process according to any one of the preceding claims wherein at least two dewaxed lubricating base oils are blended to formulate at last one lubricating oil product.

Revendications

1. Un procédé pour le déparaffinage catalytique de plus d'un précurseur d'huiles lubrifiantes de base dérivé de raffinerie, qui comprend la mise en contact dans une première zone de réaction, en présence d'un gaz contenant de l'hydrogène, dans des conditions d'hydrodéparaffinage, d'un premier courant de charge comprenant un premier précurseur d'huiles lubrifiantes de base du type raffinat dérivé de raffinerie qui contient une première cire comprenant des paraffines à chaîne droite, cette première cire contenant moins de 55 % en poids d'hydrocarbures ramifiés et cycliques, avec un premier catalyseur d'hydrodéparaffinage sélectif pour la conversion de cette première cire et la mise en contact, en présence d'un gaz contenant de l'hydrogène, dans des conditions d'hydrodéparaffinage, dans une deuxième zone de réaction située en parallèle, d'un deuxième précurseur d'huiles lubrifiantes de base du type raffinat dérivé de raffinerie qui contient une deuxième cire contenant plus de 55 % en poids d'hydrocarbures ramifiés et cycliques avec un deuxième catalyseur d'hydrodéparaffinage sélectif pour la conversion de cette deuxième cire, et éventuellement la mise en contact dans une ou plusieurs autres zones de réaction d'autres courants de charges de précurseurs d'huiles lubrifiantes de base du type raffinat cireux dérivés de raffinerie en présence d'un gaz contenant de l'hydrogène, dans des conditions d'hydrodéparaffinage, avec un catalyseur d'hydrodéparaffinage, et l'évacuation de ces zones de réaction d'au moins deux courants effluents

parallèles d'huiles lubrifiantes de base déparaffinées en raffinerie.

2. Un procédé selon la revendication 1, dans lequel les courants de charges de précurseurs d'huiles lubrifiantes de base sont obtenus en fractionnant un courant de résidu d'une distillation atmosphérique d'un courant de charge d'huile d'hydrocarbures. 5

3. Un procédé selon la revendication 1 ou 2, dans lequel les conditions de l'hydrodéparaffinage comprennent une température comprise entre 150 °C et 500 °C, une pression comprise entre 2 et 200 bars abs. et un rapport hydrogène/charge d'huile compris entre 350 et 2670 litres (T.P.N.) de H₂ par litre de charge d'huile. 10

4. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le premier catalyseur d'hydrodéparaffinage comprend une ferriérite synthétique dans laquelle est incorporé au moins un métal choisi dans le groupe constitué par les métaux du groupe VIB, du groupe VIIIB et du groupe VIII du tableau périodique. 15

5. Un procédé selon la revendication 4, dans lequel un premier courant de charge comprenant un précurseur d'huile lubrifiante cireuse HVI 80-150 ou 80-100 est hydrodéparaffiné dans la première zone de réaction à partir de laquelle une huile lubrifiante de base est obtenue sans hydrotraitement ultérieur. 20

6. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le deuxième catalyseur d'hydrodéparaffinage comprend un aluminosilicate cristallin ayant une grosseur de pores de 0,5 à 0,9 nm et une composition, en rapports molaires, telle que la suivante : 25

$0,9 \pm 0,2 M_{2/n}O : Al_2O_3 : 5-100 SiO_2 : 0-40 H_2O,$

où M est un cation et n est la valence de ce cation. 30

7. Un procédé selon l'une quelconque des revendications précédentes, qui comprend au moins trois et de préférence quatre ou plus de quatre zones d'hydrodéparaffinage catalytique situées en parallèle. 35

8. Un procédé selon l'une quelconque des revendications précédentes, dans lequel chaque catalyseur d'hydrodéparaffinage est régénéré in- 40

dépendamment de l'opération ou des opérations de déparaffinage dans l'autre ou les autres zones de réaction de déparaffinage en présence d'un gaz contenant de l'oxygène à une température comprise entre 371 °C et 566 °C. 45

9. Un procédé selon la revendication 8, dans lequel la régénération est suivie d'une purge par un gaz inerte du catalyseur régénéré et d'une réactivation ultérieure en présence d'un gaz contenant de l'hydrogène à une température comprise entre 343 °C et 538 °C. 50

10. Un procédé selon l'une quelconque des revendications précédentes, dans lequel au moins deux huiles lubrifiantes de base déparaffinées sont mélangées pour former au moins un produit huile lubrifiante de base. 55

Patentansprüche

- Ein Verfahren zum katalytischen Entwachsen von mehr als einem aus einer Raffinerieanlage stammenden Vorläufer für ein Basischmieröl, welches das Kontaktieren in einer ersten Reaktionszone in Gegenwart eines Wasserstoff enthaltenden Gases bei Entwachungsbedingungen eines ersten Zuspeisungsstroms, enthaltend einen ersten aus einer Raffinerieanlage stammenden Basischmieröl-Vorläufer in Form eines Raffinats, welcher ein erstes Wachs, umfassend geradkettige Paraffine, enthält, wobei das erste Wachs weniger als 55 Gewichtsprozent an verzweigten und zyklischen Kohlenwasserstoffen enthält, mit einem ersten Entwachungskatalysator, welcher für die Umwandlung des genannten ersten Wachsese geeignet ist, und das Kontaktieren in Gegenwart eines Wasserstoff enthaltenden Gases bei Hydroentwachungsbedingungen in einer parallel angeordneten zweiten Reaktionszone eines zweiten aus einer Raffinerieanlage stammenden Basischmieröl-Vorläufers in Form eines Raffinats, welcher ein zweites Wachs, enthaltend mehr als 55 Gewichtsprozent an verzweigten und zyklischen Kohlenwasserstoffen enthält, mit einem zweiten Hydroentwachungskatalysator, welcher für die Umwandlung des genannten zweiten Wachsese geeignet ist, und gegebenenfalls das Kontaktieren von weiteren aus Raffinerieanlagen stammenden wachshaltigen Basischmieröl-Vorläuferzuspeisungsströmen in Form von Raffinaten in einer oder mehreren Reaktionsstufe(n) in Gegenwart eines Wasserstoff enthaltenden Gases bei Hydroentwachungsbedingungen mit einem Hydroentwachungskatalysator, und das Abziehen

mindestens zwei paralleler Abflußströme in Form von Raffinerie- entwachsen Basis- schmierölen aus den genannten Reaktionszo- nen umfaßt.

2. Ein Verfahren nach Anspruch 1 , in welchem die Basisschmieröl-Vorlä- uferzuspeisungsströme durch Fraktionieren ei- nes Bodenstroms aus einer atmosphärischen Destillation eines Kohlenwasserstoffölzuspei- sungsstroms erhalten werden.

3. Ein Verfahren nach Anspruch 1 oder 2, in welchem die Hydroentwachungsbedingungen eine Temperatur zwischen 150 °C und 500 °C, einen Druck zwischen 2 und 200 bar abs. und ein Wasserstoff/Öl-Zuspeisungsverhältnis zwi- schen 350 und 2670 l(S.T.P) H₂/l Ölzu- spei- sung umfassen.

4. Ein Verfahren nach einem der vorstehenden Ansprüche, in welchem der erste Hydroent- wachungskatalysator einen synthetischen Fer- rierit umfaßt, in welchem mindestens ein Me- tall, ausgewählt aus Metallen der Gruppe, be- stehend aus Gruppe VIIB, Gruppe VIIIB und Gruppe VIII des Periodischen Systems der Elemente, integriert ist.

5. Ein Verfahren nach Anspruch 4, in welchem ein erster Zuspeisungsstrom, umfassend einen wachshaltigen HVI 80 bis 150 oder 80 bis 100 Schmierölvorläufer , in der ersten Reaktionszo- ne hydroentwächst wird, aus welcher ohne an- schließende Hydrobehandlung ein Basis- schmieröl erhalten wird.

6. Ein Verfahren nach einem der vorstehenden Ansprüche, in welchem der zweite Hydroent- wachungskatalysator ein kristallines Alumino- silikat mit einer Porengröße von 0,5 bis 0,9 nm und einer Zusammensetzung, ausgedrückt in Molverhältnissen, wie folgt, umfaßt:

0,9 + 0,2 M_{2/n}O: Al₂O₃:5-100 SiO₂:0-40 H₂O, wobei M ein Kation ist und n die Wertigkeit dieses Kations bedeutet.

7. Ein Verfahren nach einem der vorstehenden Ansprüche, welches mindestens 3 und vor- zugsweise 4 oder mehr parallel angeordnete Zonen zum katalytischen Hydroentwachsen umfaßt.

8. Ein Verfahren nach einem der vorstehenden Ansprüche, in welchem jeder Hydroentwach- sungskatalysator unabhängig von dem(den)

Entwachungsvorgang(bzw.-Vorgängen) in der- (den) anderen Entwachungszone(n) in Gegen- wart eines sauerstoffhaltigen Gases bei einer Temperatur von 371 °C bis 566 °C regeneriert wird.

9. Ein Verfahren nach Anspruch 8, in welchem auf die genannte Regenerierung eine Spülung des regenerierten Katalysators mit Inertgas und eine anschließende Reaktivierung in Ge- genwart eines wasserstoffhaltigen Gases bei einer Temperatur von 343 °C bis 538 °C folgt.

10. Ein Verfahren nach einem der vorstehenden Ansprüche, in welchem mindestens zwei ent- wachste Basisschmieröle vermischt werden, um schließlich ein Schmierölprodukt zu erhal- ten.

